

Production and Storage of Hydrogen Using C1 Chemistry

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Consortium for Fossil Fuel Science (CFFS)

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Project ID #: PDP 29

Overview

Timeline

- Start: June 2, 2005
- End: June 1, 2008
- 28 % complete

Budget

- Total project funding
 - DOE - \$6,000,000
 - CFFS - \$1,500,000
- Funding received in FY05 - \$2,000,000

Barriers

- Produce hydrogen from coal with minimum CO₂ production.
- Hydrogen storage/carrier media.

Partners

CFFS: U of Kentucky, West Virginia U, U of Pitts., U of Utah, Auburn U

Advisory Board: Eastman, ConocoPhillips, Chevron, Texaco, US Air Force, US Army

Objectives

- Develop innovative technology for producing hydrogen from coal-derived syngas or from hydrogen rich liquids and gases produced from coal-derived syngas.
- Develop better methods of producing hydrogen-rich liquids and gases from coal.

Approach

The Consortium for Fossil Fuel Science includes professors and students from five universities – **Kentucky, West Virginia, Pitt, Auburn, and Utah.** They are conducting a collaborative research program focused on the production of hydrogen and clean hydrogen-rich liquids and gases from coal using **C1 chemistry.**

Accomplishments

Because this is a new contract, most of the research projects being addressed have been underway for less than a year. One exception is a project at the University of Kentucky dealing with the production of hydrogen by **Non-Oxidative Catalytic Dehydrogenation**, which began in our previous DOE contract and continued into the current program. This project will be the primary focus of this presentation and its accomplishments will be discussed in detail. Accomplishments of the other, newer, research projects in the CFFS hydrogen research program will be summarized more briefly.

Accomplishments – Catalytic Dehydrogenation

- Binary Fe-M (4.5%Fe-0.5%M/ Al_2O_3 , M=Ni, Mo, or Pd) catalysts have excellent activity and lifetimes for non-oxidative dehydrogenation of gaseous alkanes, yielding pure hydrogen in one step. No CO or CO_2 is produced.
- Carbon is produced primarily in the form of nanotubes. Multi-walled nanotubes (MWNT) are dominant but stacked-cone nanotubes (SCNT) are easily produced by varying the temperature and feed gas.
- A continuous process for catalytic dehydrogenation of methane using these catalysts was developed using a mixed-mode, fluid-bed/fixed bed, reactor.

Accomplishments – Catalytic Dehydrogenation

- Mössbauer and XAFS spectroscopy indicate that the active phase is an Fe-M-C austenitic alloy bound to the alumina by an Fe-aluminate, hercynite.
- Fe-M alloy catalysts on Mg-Al oxide have been tested. Although the hydrogen production is lower, the nanotubes are easily cleaned by dissolving the support.
- Pt nanoparticles on SCNT are excellent catalysts for stripping hydrogen from high hydrogen content liquids (cyclohexane, tetralin, decalin, etc.) leaving rechargeable aromatic phases.

Accomplishments of newer CFFS projects

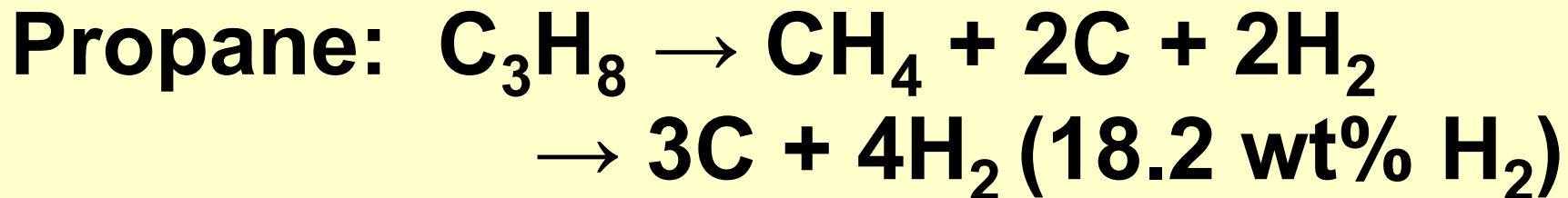
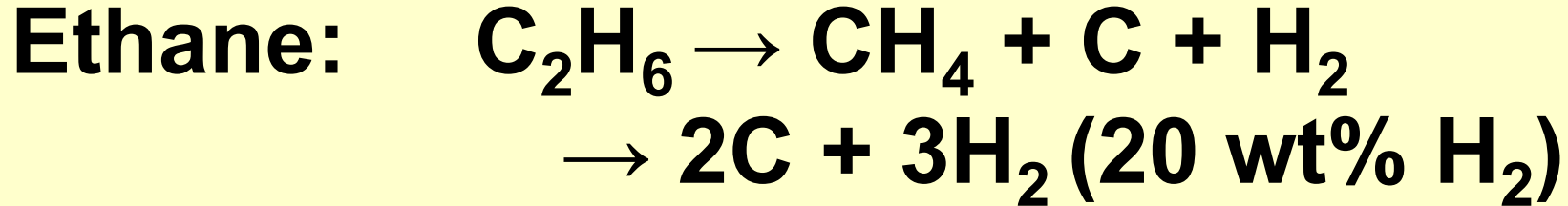
- A process for co-production of hydrogen and methyl formate from methanol has been developed. **U. of Pittsburgh**
- Promising catalysts for the water-gas shift (WGS) reactions were prepared by gas phase deposition of dispersed Pd nanoparticles on ceria aerogels. **U. of Utah**
- Low temperature aqueous reforming of ethylene glycol and other polyols yields large percentages of hydrogen with very little CO. **U. of Pittsburgh**
- Reforming of methanol in supercritical water yields ~98% H₂ with CO and CO₂ percentages <2 %. **Auburn U.**

Accomplishments of newer CFFS projects

- Partial oxidation of propane was investigated using Pt/CeO₂ catalysts. Proper adjustment of operating parameters were shown to yield a hydrogen-rich syngas. ***West Virginia U.***
- Projects focused on the production of hydrogen-rich liquid fuels via the Fischer-Tropsch (F-T) synthesis reaction are ongoing at all of the five CFFS universities and are discussed in a recent report and many publications that are available at our web site – www.cffs.uky.edu .

Catalytic dehydrogenation

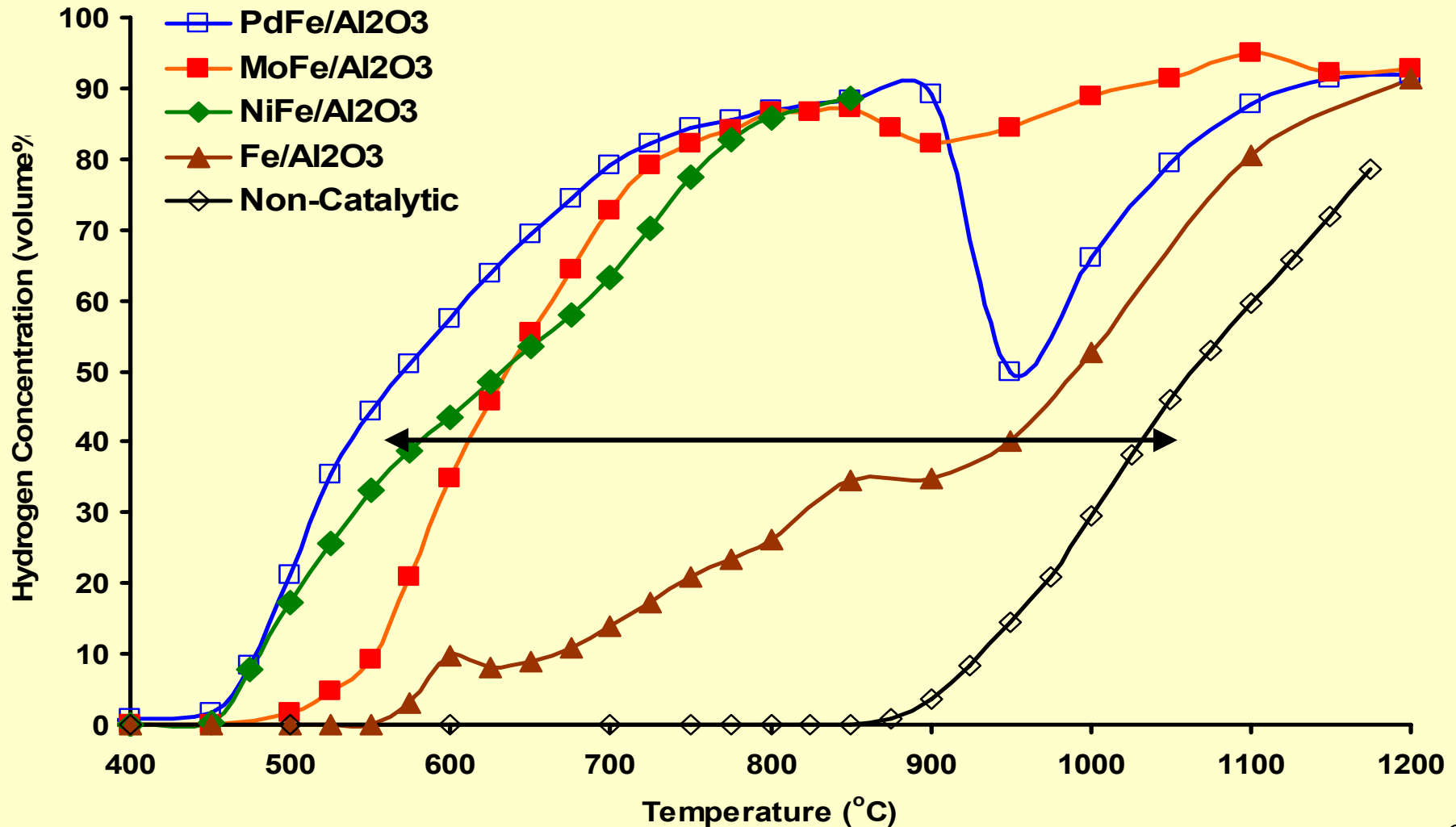
The remainder of this presentation presents a more detailed summary of CFFS research on catalytic dehydrogenation. The reactions of interest for gases are given below.



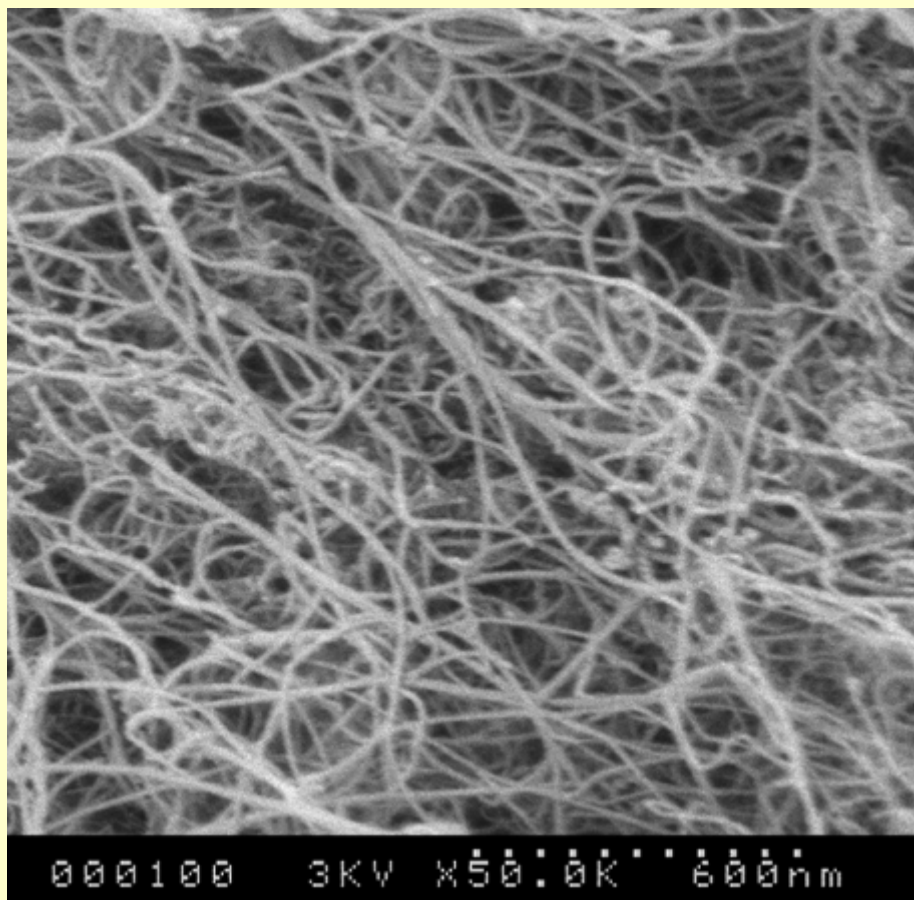
Catalysts Employed

- Binary Fe-based catalysts (0.5%M-4.5%Fe)/ γ -Al₂O₃ (M=Mo, Ni, or Pd)
- Prepared by co-precipitation and incipient wetness methods.
- Pre-reduced in hydrogen at 700 °C for 2 hrs in situ in reactor.

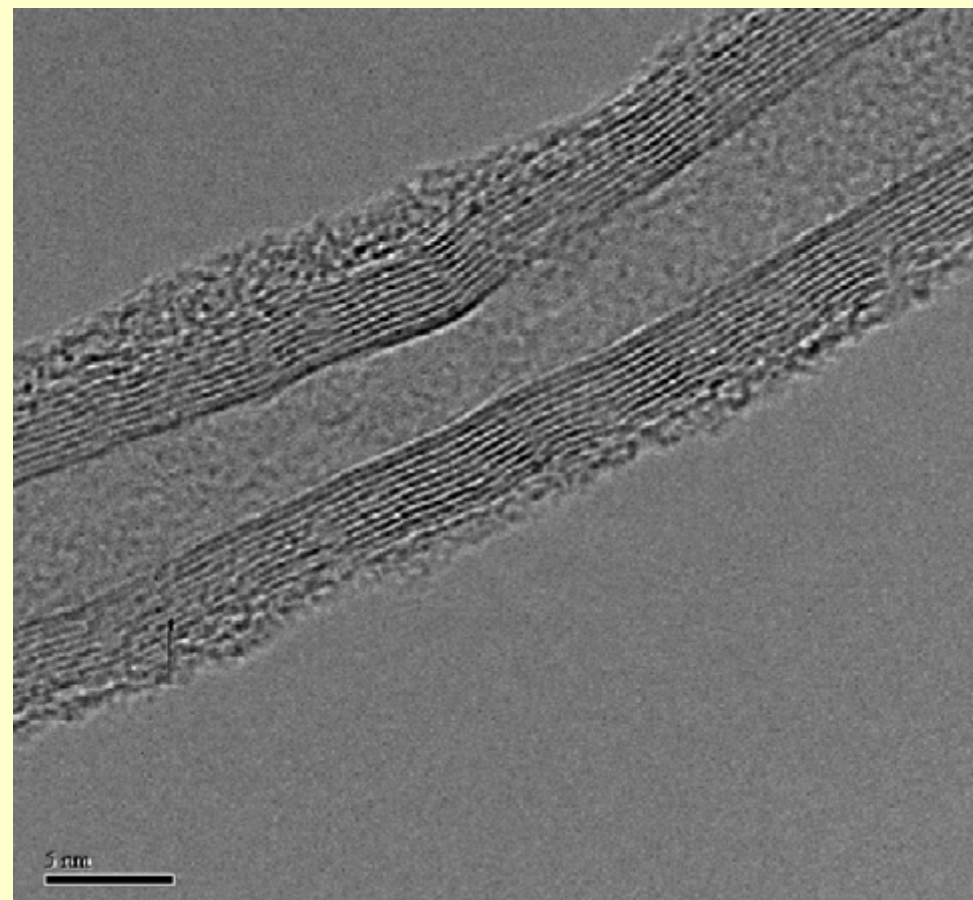
Catalytic Dehydrogenation of Methane



Decomposition temperatures are lowered by 450-500 °C.
Hydrogen production is maximized at ~700-800 °C



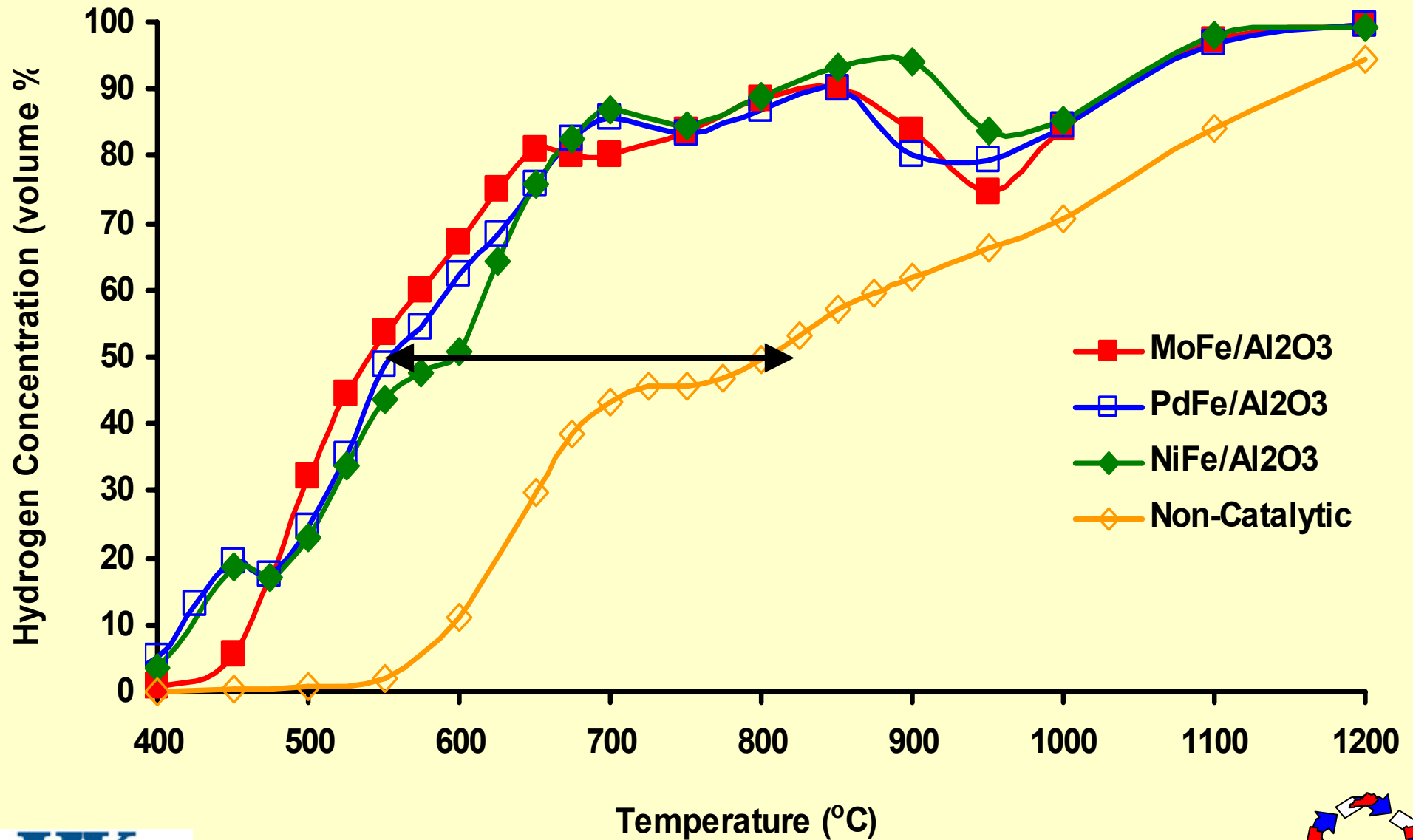
500 nm

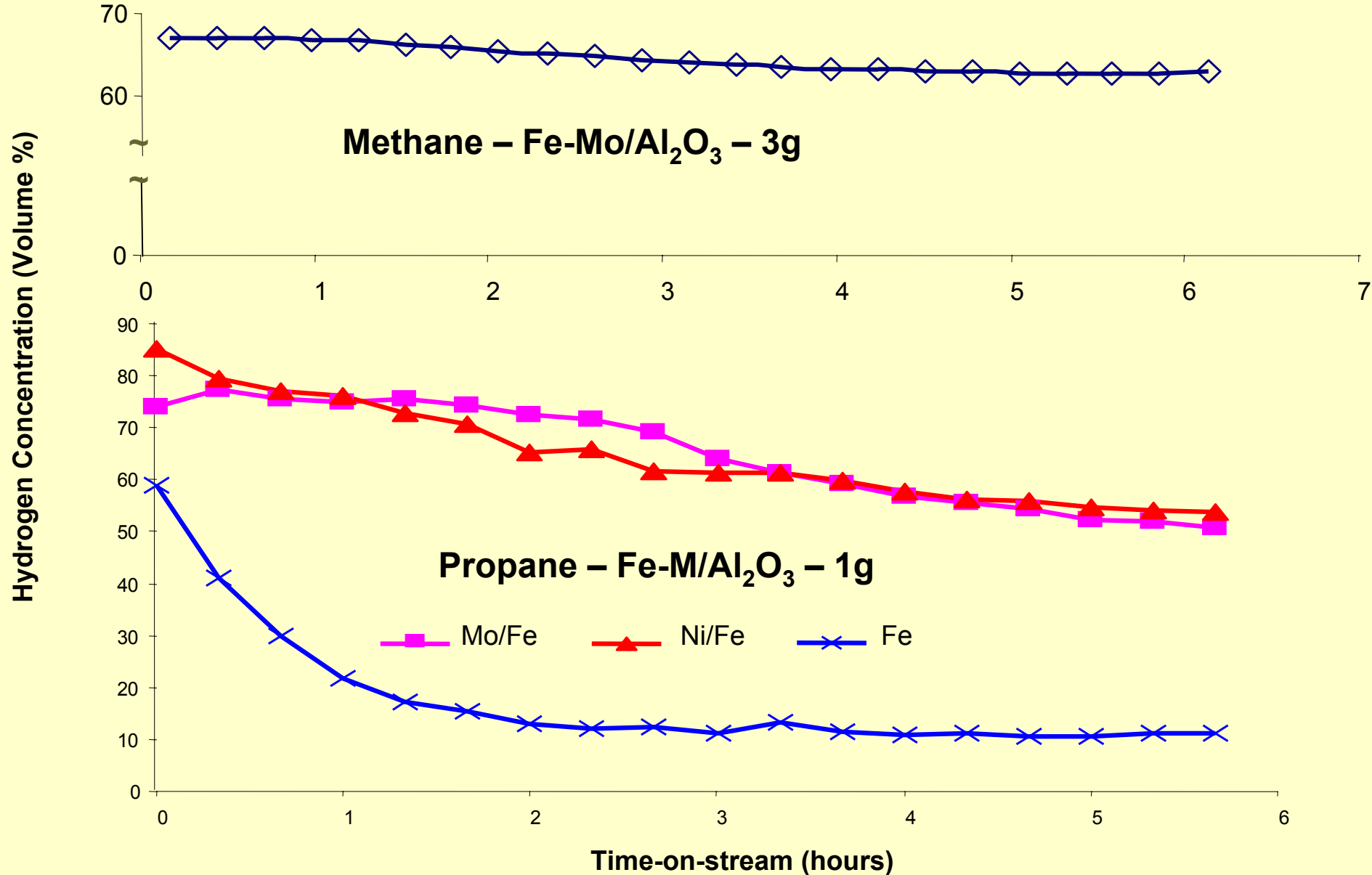


5 nm

SEM and HRTEM of carbon nanotubes (MWNT)
 produced by decomposing undiluted methane at 700 °C
 over 0.5%Mo-4.5%Fe/ γ -Al₂O₃ pre-reduced at 700 °C

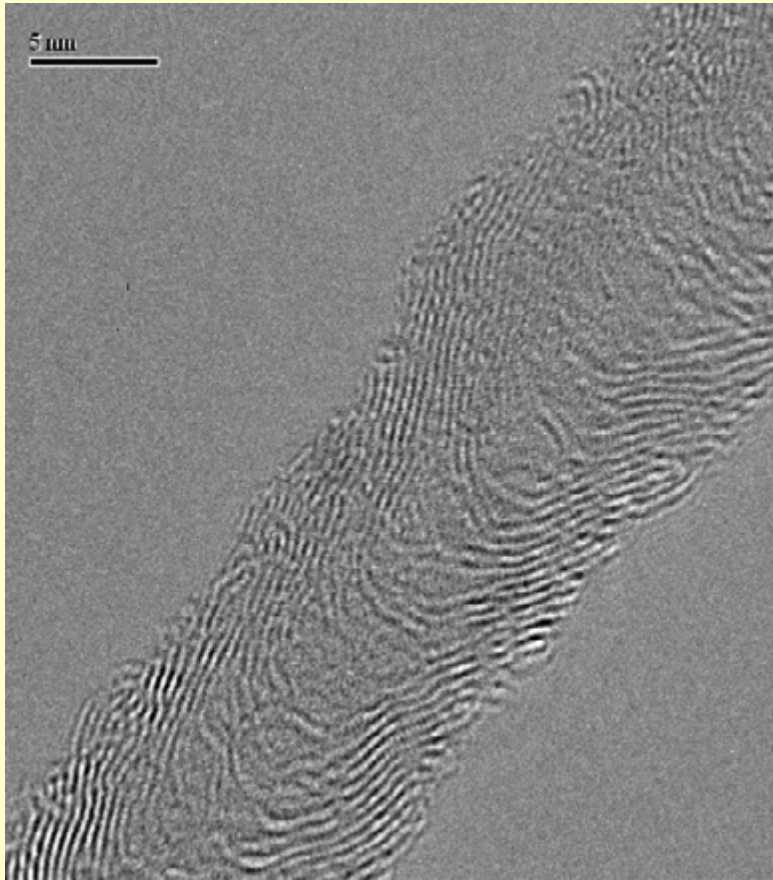
Catalytic decomposition of Ethane



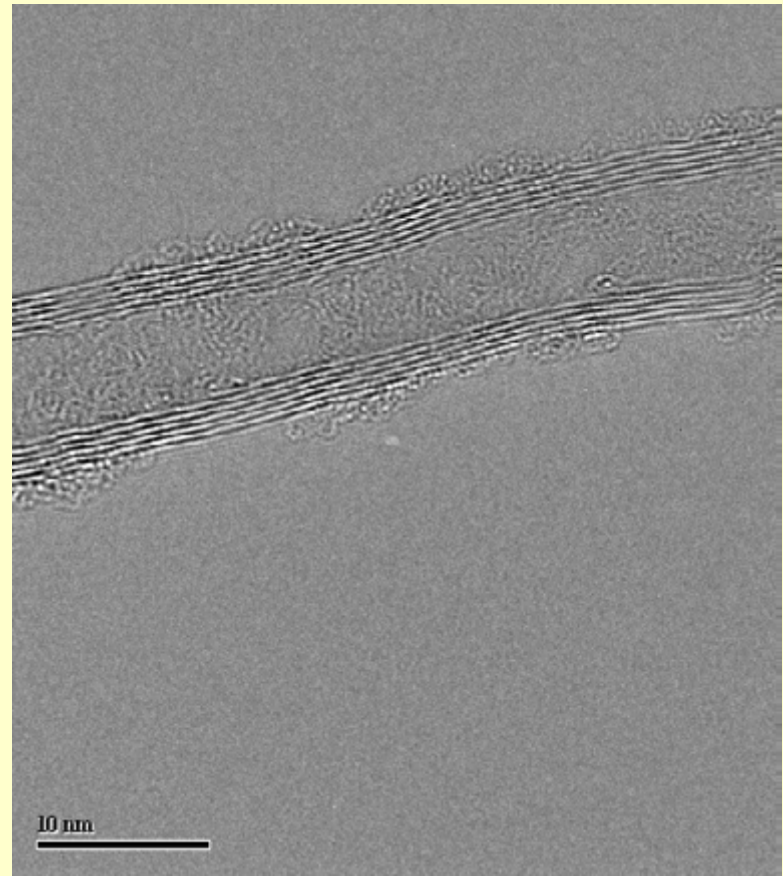


The catalysts exhibit reasonably good lifetimes, with deactivation rates of ~1-5% per hour in a plug-flow reactor.

Stacked-cone nanotubes (SCNT) are produced from propane and ethane below 500 °C and multi-walled nanotubes (MWNT) above 600 °C.



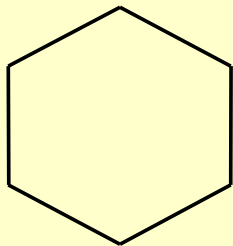
SCNT



MWNT

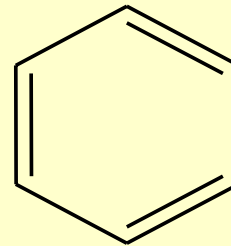
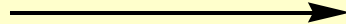
Fuel cell vehicles (FCV) require a high-hydrogen content liquid fuel as a hydrogen carrier

Examples: cyclohexane (7.1 wt.%)
methyl cyclohexane (6.5 wt.%)
decalin (7.2 wt. %)



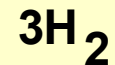
Cyclohexane
1 mole

Catalysts

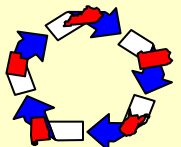


Benzene
1 mole/25%

+

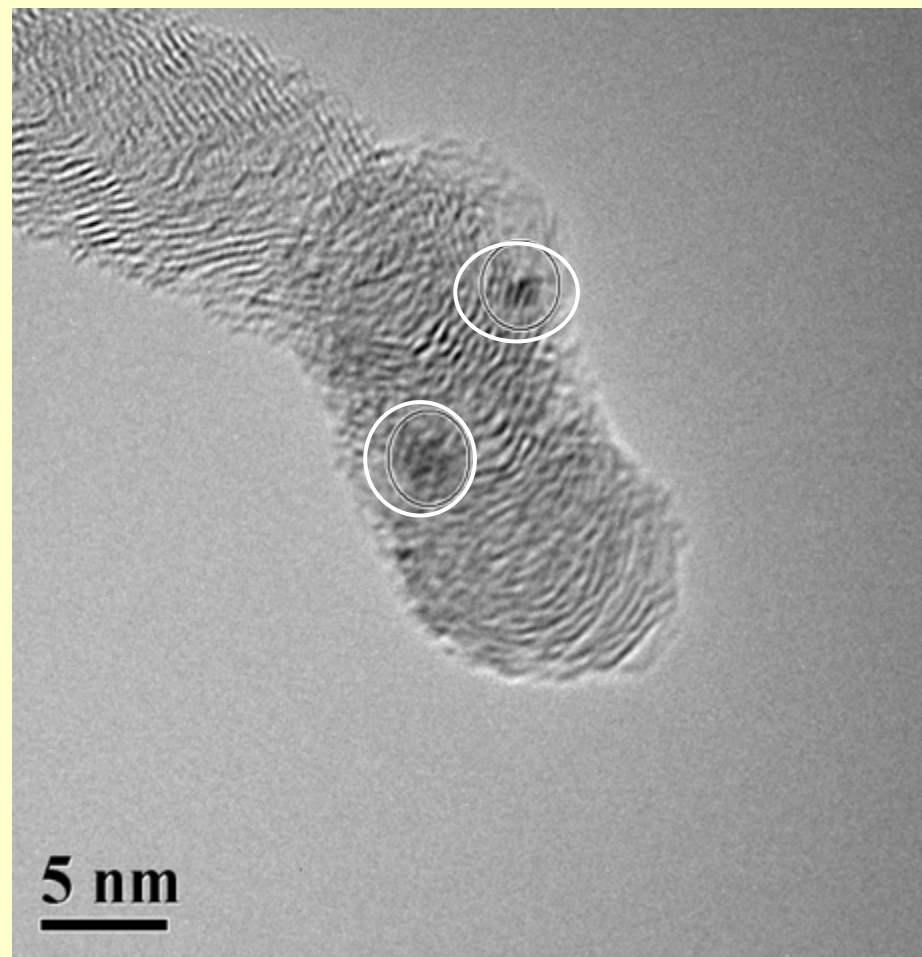
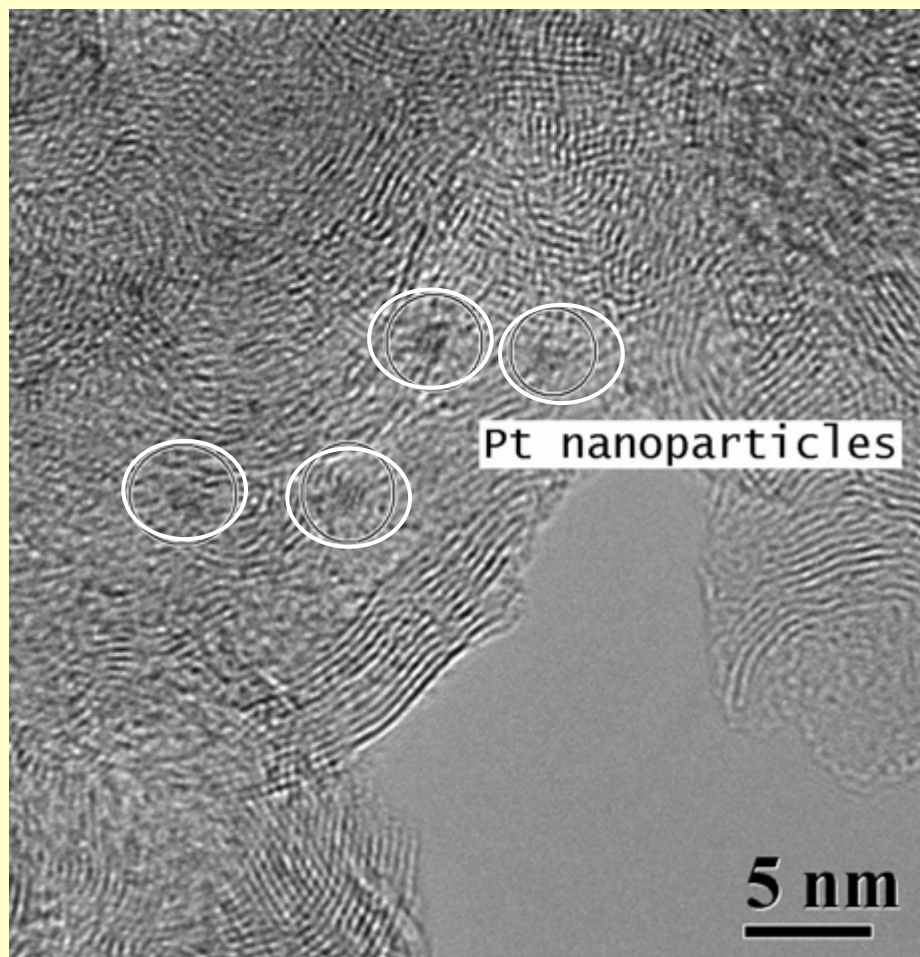


Hydrogen
3 moles/75%

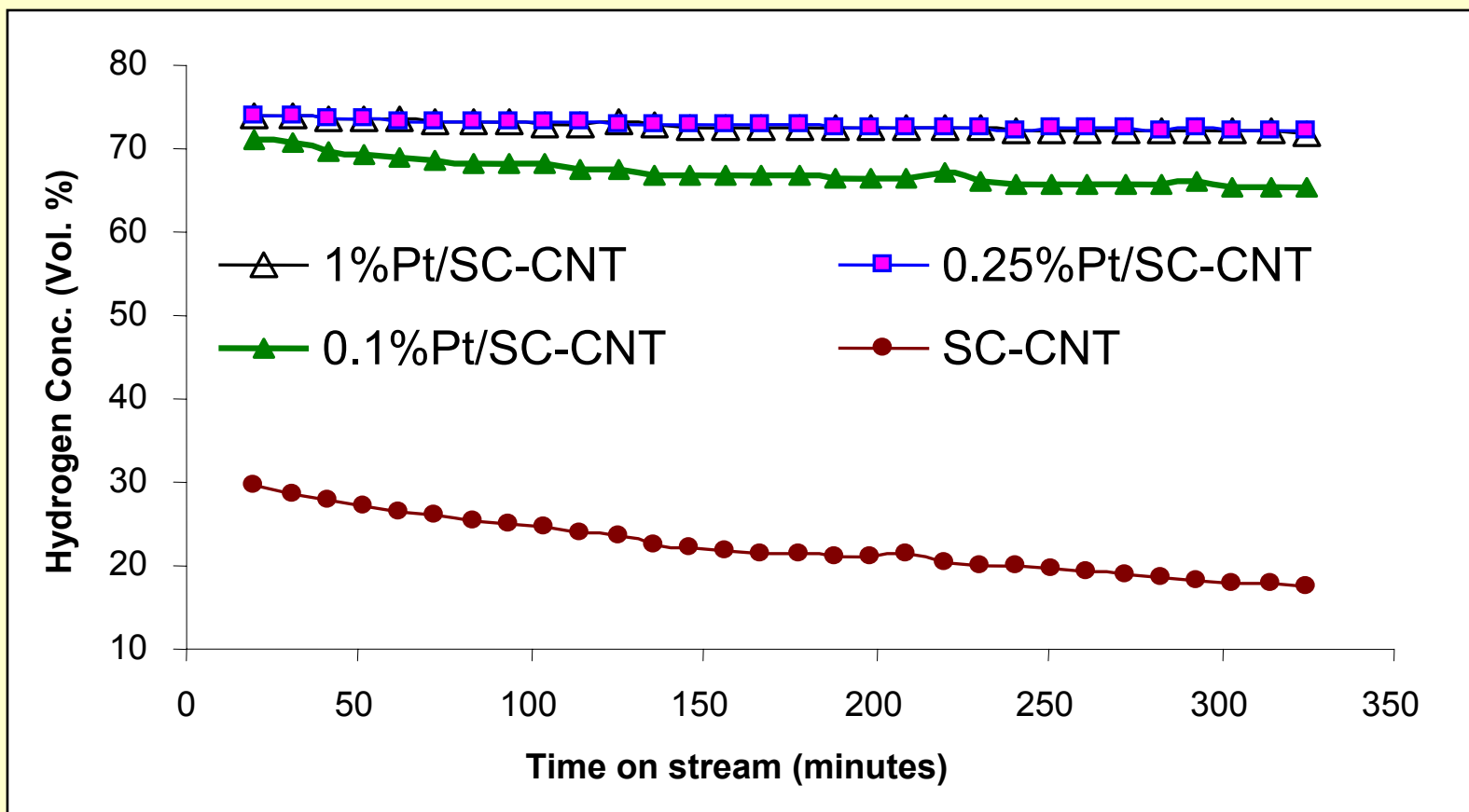


CFFS

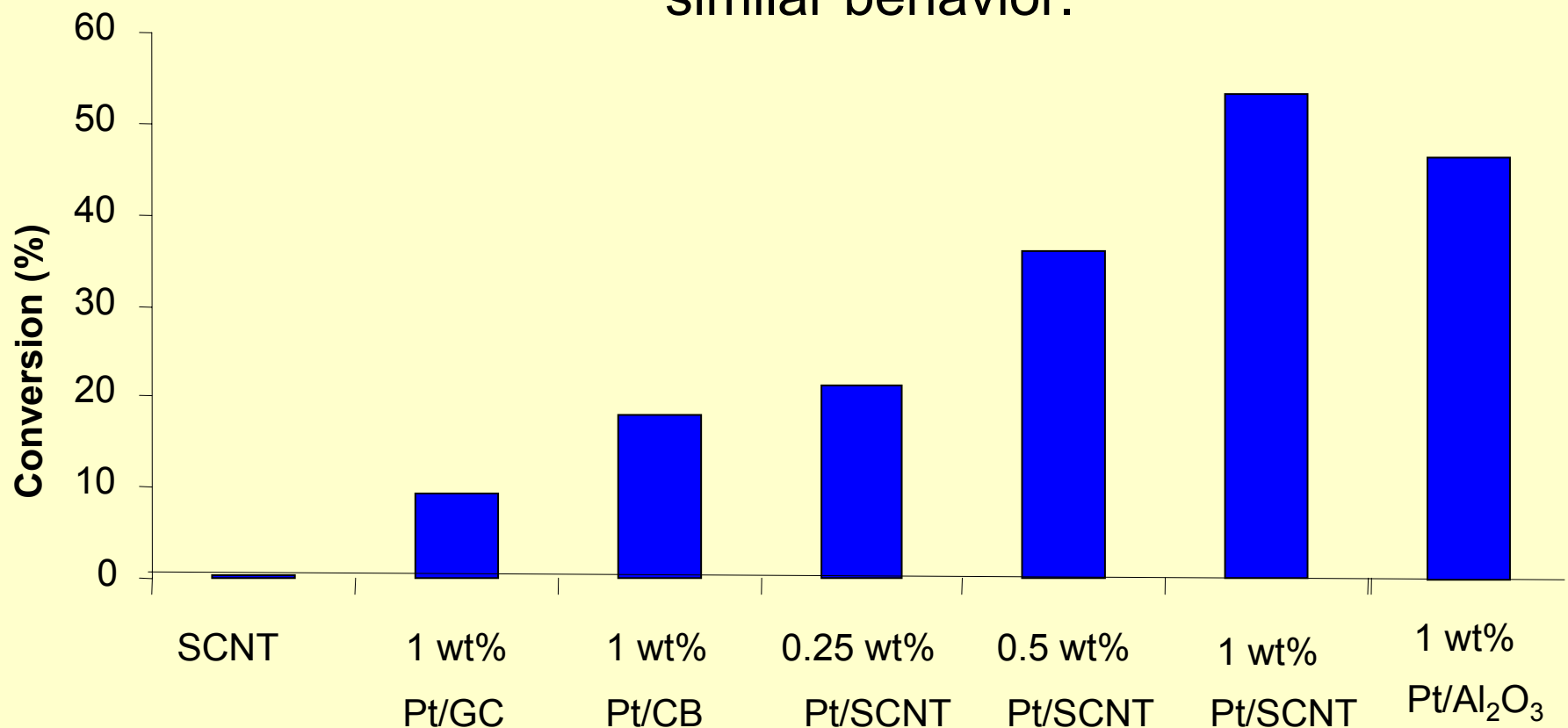
HRTEM of used catalysts 1%Pt/SCNT after dehydrogenation of cyclohexane at 315 °C. Note that the size of the Pt nanoparticles is only ~2-3 nm.



Hydrogen production from cyclohexane at 315 °C by Pt/SCNT catalysts. 75 vol.% hydrogen represents conversion of cyclohexane to benzene and hydrogen. Similar results were obtained for methylcyclohexane.



Comparison of Pt/SCNT to Pt on other supports
(Al_2O_3 , granular carbon/GC, and carbon black/CB) for
tetralin dehydrogenation at 240 °C. Decalin shows
similar behavior.



Summary

- Catalytic dehydrogenation is an alternative one-step method of producing pure hydrogen from hydrocarbon gases and liquids that produces no CO or CO₂. All carbon is produced as a potentially valuable by-product, carbon nanotubes.
- Although production of carbon nanotubes is preferable to producing carbon dioxide, large scale uses for nanotubes could make the process much more appealing.
- Partial catalytic dehydrogenation of liquid hydrocarbons may be a viable method of producing hydrogen on-board in vehicles, particularly if high hydrogen content liquids can be synthesized that can be dehydrogenated at $<\sim 100\text{ }^{\circ}\text{C}$.

Future Work

- Develop new supports for Fe-M dehydrogenation catalysts that are easily dissolved and have good activity and lifetimes.
- Develop synthesis processes for monodisperse metallic nanoparticles (~5 nm) for dehydrogenation applications, both as supported and as unsupported catalysts (late 2006).
- Develop a continuous dehydrogenation reactor that utilizes unsupported nanoparticle catalysts and includes a spooling process for nanotube collection (2007).
- Develop liquids for vehicular applications that can be catalytically dehydrogenated/hydrogenated at ~100 °C (2007).
- Explore large scale uses for nanotubes; one possibility is as environmental sorbents.

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Publications and Presentations

14. A. Punnoose, N. Shah, G.P. Huffman, and M.S. Seehra, “X-ray diffraction and electron magnetic resonance studies of M/Fe/Al₂O₃ (M=Ni, Mo, and Pd) catalysts for CH₄ to H₂ conversion”, *Fuel Processing Technology*, **83** (2003) 263-274.
15. Alex Punnoose, T. Phanthavady, M.S. Seehra, N. Shah, and G.P. Huffman, “Magnetic properties of ferrihydrite nanoparticles doped with Ni, Mo, and Ir”, *Phys. Rev. B*, **69** (2004), 054425-054434.
16. Naresh Shah, Yuguo Wang, Devadas Panjala, Gerald P. Huffman; [Hydrogen and carbon nanostructures production by non-oxidative catalytic dehydrogenation of ethane and propane](#), *Energy & Fuels*, **18**(3), (2004) 727-735.
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